

## **SPECIFICATION**

### **1. Title of the Invention**

**Method for the ambient temperature curing of thermosetting resins**

### **2. Claim**

#### **Claim 1.**

Version from Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number Sho 60-090251 (the A document)

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Method for the ambient temperature curing of thermosetting resins, characterized in that curing is effected at ambient temperature by means of the addition of ethylene carbonate and base to thermosetting resin.

Version from Japanese Published (Examined or Kokoku or B) Patent Application Number Hei 07-088460 (the B document)

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Method for the ambient temperature curing of thermosetting resins, characterized in that curing is effected at ambient temperature by means of the addition of ethylene carbonate and base to thermosetting resin that contains phenolic OH.

### **3. Detailed Description of the Invention**

The invention relates to a method for the ambient temperature curing of thermosetting resins. More particularly, the invention relates to a method for the ambient temperature curing of thermosetting resins, wherein said method enables free control of the cure rate, is easy to carry out, and has a broad range of application.

Thermosetting resins cure by the application of heat, as the name implies, and are in wide use. However, the cure of thermosetting resins at or near ambient temperature has recently come under investigation in support of efforts at energy conservation and in order to enable application with materials that cannot be heated.

The acid curing method is the most widely known ambient temperature curing method. Acid curing is a method in which the resin is polymerized and crosslinked using an acid such as p-toluenesulfonic acid. The cure rate can be adjusted in the acid curing method by adjusting the type and amount of acid that is added. However, since this method employs acid, when a basic substance is used for the backbone substance, reaction between the acid and basic substance proceeds preferentially and an inadequate cure is produced. Moreover, acid curing cannot be used to cure structures in contact with metal due to the corrosiveness exercised by the acid. Another problem is that acid-cured resins generally have a low impact strength and are brittle. Acid curing also requires the use of large amounts of strong acid to raise the cure rate, and the curing reaction, once started, proceeds with increasing velocity since acid-induced curing reactions are accompanied by the generation of large amounts of heat. This facilitates the generation of pores in the cured product and in some cases is also hazardous. These factors place limits on the extent to which the cure rate can be raised.

The isocyanate curing method, which has reached the level of practical application, improves upon the problems identified above. Isocyanate curing uses an isocyanate as the curing agent and uses a tertiary amine as a cure accelerator. While the isocyanate curing method is an excellent curing method, it yields a cured product that contains the urethane bond, which forfeits the excellent heat resistance that is an advantage of thermosetting resins. In addition, the tertiary amine cure accelerator (e.g., triethylenediamine, N-alkylformalin) is frequently toxic and must be handled in a sealed system. Moreover, when used with a mold, the evolution of cyanide has been reported due to thermal degradation of the isocyanate curing agent. Thus, the isocyanate curing method also cannot be said to be entirely satisfactory.

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Version from the A document

This invention was achieved as a result of various investigations, taking into account the circumstances noted above, into the ambient temperature curability of thermosetting resins. The object of this invention is to provide a method for the ambient temperature curing of thermosetting resins, wherein said method does not require special handling equipment and enables free control of the cure rate.

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Version from the B document

This invention was achieved as a result of various investigations, taking into account the circumstances noted above, into the ambient temperature curability of thermosetting resins and particularly thermosetting resins bearing phenolic OH, such as the widely used phenolic resins. The object of this invention is to provide a method for the ambient temperature curing of thermosetting resins bearing phenolic OH, wherein said method does not require special handling equipment and enables free control of the cure rate.

The inventive method, through its use of ethylene carbonate as the curing agent for thermosetting resin and the addition of base as a cure accelerator, achieves the ambient temperature cure of thermosetting resin and makes possible free control of the cure rate.

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The most significant advantage of the ethylene carbonate curing agent used by this invention is that it makes possible an extremely broad-ranging control of the cure time — from approximately 1 minute at the shortest to 24 hours or more — through selection of the type and quantity of addition of the base used as cure accelerator. In addition, unlike the circumstances with acid curing, a sharp exothermic reaction is not encountered even when curing is carried out very rapidly in a brief 1-2 minutes.

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It is believed that ring-opening of the ethylene carbonate curing agent is promoted by the action of the base used as cure accelerator and that curing at ambient temperature proceeds through the reaction of the ring-opened ethylene carbonate with the thermosetting resin, resulting in polymerization and crosslinking.

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The most significant advantage of the ethylene carbonate curing agent used by this invention is that it makes possible an extremely broad-ranging control of the cure time at around ambient temperature — from approximately 1 minute at the shortest to 24 hours or more — based on selection of the type and quantity of addition of the base used as cure accelerator. In addition, unlike the circumstances with acid curing, a sharp exothermic reaction is not encountered even when curing is carried out very rapidly in a brief 1-2 minutes.

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It is believed that the base used as cure accelerator acts even at ambient temperature to promote ring-opening of the ethylene carbonate curing agent through elimination of the carbonate group and that curing at ambient temperature proceeds through reaction of the ring-opened ethylene group with terminal methylol and hydrogen on benzene activated by the effect of the OH group in the phenolic OH-bearing thermosetting resin, resulting in polymerization and crosslinking.

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The thermosetting resin used by the invention can be exemplified by phenolic resins, furan resins, urea resins, melamine resins, and so forth, among which resole-type phenolic resins, furan resins, and modified resins therefrom are preferred.

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The phenolic OH-bearing thermosetting resin used by the invention can be exemplified by phenolic resins, furan resins, and modified resins therefrom, among which phenolic resins are preferred.

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Ethylene carbonate is used as the inventive curing agent. It is added at 1-100 weight parts and preferably 2-80 weight parts per 100 weight parts thermosetting resin. Thorough development of the curing reaction is not obtained at an ethylene carbonate addition of less than 1 weight part, and as a result the obtained cured product will not exhibit satisfactory strength. The addition of more than 100 weight parts is undesirable for the following reasons: the cure is unchanged at additions greater than 100 weight parts, making such additions uneconomical; also, the ethylene carbonate that does not participate in the curing reaction will function as a solvent, resulting in a porous cured product that exhibits poor strength.

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Ethylene carbonate is used as the inventive curing agent. It is added at 1-100 weight parts and preferably 2-80 weight parts per 100 weight parts of the phenolic OH-bearing thermosetting resin. Thorough development of the curing reaction is not obtained at an ethylene carbonate addition of less than 1 weight part, and as a result the obtained cured product will not exhibit satisfactory strength. The addition of more than 100 weight parts is undesirable for the following reasons: the cure is unchanged at additions greater than 100 weight parts, making such additions uneconomical; also, the ethylene carbonate that does not participate in the curing reaction will function as a solvent, resulting in a porous cured product that exhibits poor strength.

There are no restrictions on the base used as the cure accelerator as long as it exhibits basicity in water or organic solvent, and this base can be exemplified by the hydroxides and carbonates of alkali metals (e.g., NaOH, K<sub>2</sub>CO<sub>3</sub>, etc.), the oxides and hydroxides of alkaline-earth metals (e.g., MgO, Ca(OH)<sub>2</sub>, etc.), and organic bases such as amines, etc. The use of a strong base results in a high cure rate, while the use of a weak base results in gentle cure development. The type and quantity of addition of the base may therefore be selected based on the required cure rate. While the quantity of base addition is determined in light of the type selected based on the desired cure rate as discussed above, the use of 3-300 weight parts per

100 weight parts ethylene carbonate is desirable. Lower additions in the range of 3-150 weight parts are appropriate for strong bases, while larger additions in the range of 30-300 weight parts are appropriate for weak bases. Resole-type phenolic resins are produced by the base-catalyzed reaction of phenol and formaldehyde followed by neutralization by the addition of acid. Ambient temperature curing can also be achieved without the specific addition of base through the direct use of resole-type phenol resin that has not been subjected to acid neutralization. The cure rate can be controlled even in this case by promoting cure by the further addition of base or by inhibiting cure by a less-than-exhaustive addition of acid.

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Version from the A document

The A document does not contain a corresponding paragraph.

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Version from the B document

When, for example, magnesium [sic] or calcia is present in microparticulate form in the material to be cured, for example, molding material, use of the base compound may be omitted. However, in the event of a slow cure rate, the base compound may be added in order to adjust the rate.

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A characteristic feature of the inventive method for curing thermosetting resin is the use of ethylene carbonate as curing agent and base as cure accelerator in order to bring about ambient temperature curing. However, it is also possible to carry out curing at temperatures above ambient temperature.

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A characteristic feature of the inventive method for curing phenolic OH-bearing thermosetting resin is the use of ethylene carbonate as curing agent and base as cure accelerator in order to bring about ambient temperature curing. However, it is also possible to carry out curing at temperatures above ambient temperature.

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Version from the A document

The content of the invention is described below using examples, but the inventive method for the ambient temperature curing of thermosetting resin is not limited by these examples.

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Version from the B document

The content of the invention is described below using examples, but the inventive method for the ambient temperature curing of phenolic OH-bearing thermosetting resin is not limited by these examples.

**Examples 1-5**

Curing tests at ambient temperature (18°C) were carried out by the combination of resole-type phenolic resin (specific gravity = 1.19, 59% nonvolatile fraction, viscosity = 85 cP at 25°C, pH = 7.1), ethylene carbonate, and base in the amounts reported in Table 1 with 100 weight parts silica. The tests were carried out by mixing/kneading the blend using a Waring mixer, molding immediately after dust discharge to 50 × 50 × 50 mm, and curing after molding. The time required to reach a compressive strength of 20 kg/cm<sup>2</sup> was measured and designated the cure time. The results are reported in Table 1.

Table 1.

example no.	1	2	3	4	5
addition in weight parts					
phenolic resin	2	2	2	2	2
ethylene carbonate	0.5	1	1	1.5	1
base	50% aq. NaOH solution 1	50% aq. NaOH solution 0.2	Ca(OH) <sub>2</sub> 1	MgO 1	MgO 0.5
cure time	1.5 min	10 min	1.5 hr	5 hr	24 hr

As shown in the preceding examples, the inventive curing method enables a thorough cure at ambient temperature and also makes it possible to adjust the cure time over a very broad range.

**Examples 6-9**

Casting was carried out at ambient temperature after the combination of unneutralized resole-type phenolic resin (specific gravity = 1.16, nonvolatile fraction = 42%, viscosity = 95 cP at 25°C, pH = 11.4) with 100 parts calcium carbonate filler. The additives other than calcium carbonate and their quantities of addition are reported in Table 2. After the blend had been mixed/kneaded with a kneader, it was poured into a 50 Ø × 50 H mm shape. The cure time was the time required to reach a compressive strength of 20 kg/cm<sup>2</sup> and is reported in Table 2.

Table 2.

example no.	6	7	8	9
addition in weight parts				
phenolic resin	40	40	40	40
ethylene carbonate	2	2	2	2
cure-adjustment agent	50% aq. NaOH solution 0.5	—	primary sodium phosphate 0.6	boric acid 1
cure time	20 min	50 min	5 hr	12 hr

As the preceding examples make clear, the inventive curing method is entirely practical even when the thermosetting resin is used as a casting material and still enables control of the cure rate.